

# Exploratory Studies of Novel Sodium-ion battery systems

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Xiao-Qing Yang and Xiqian YU  
Brookhaven National Lab. (BNL)

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# Overview

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## Timeline

- **Start: 10/01/2015**
- **Finish: 09/30/2018**

## Budget

- **Funding received in FY15**  
**DOE: \$500k**
- **Funding received in FY16**  
**DOE: \$500k**

## Barriers addressed

- To reduce the production cost of a PHEV battery
- Na-ion and Na-metal batteries with long calendar and cycle life
- Na-ion and Na-metal batteries with superior abuse tolerance

## Collaborators

- University of Texas-Austin
- Drexel University
- Massachusetts Institute of Technology (MIT)
- University of Maryland at College Park
- Lawrence Berkeley National Laboratory (LBNL)
  
- Institute of Physics, Chinese Academy of Sciences
- Institute of Chemistry, Chinese Academy of Sciences
- Beijing Institute of Technology

# Relevance and Project Objectives

✓ *Diagnostics study of thermal abuse tolerance (to improve the safety characteristics of electrode materials for Na-ion batteries).*

- to do comparative studies of thermal stability between the  $\text{LiCoO}_2$  and  $\text{NaCoO}_2$  cathode materials to understand the structural origin of them.
- to establish and investigate the structural changes of new tunnel structured  $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$  as anode material for Na-ion batteries during charge-discharge cycling
- to evaluate and study the electrochemical performance of a new O3-type layer-structured metal oxide cathode  $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$  for sodium ion batteries.
- to provide valuable information about how to design thermally stable cathode materials for Na batteries for HEV and PHEV applications.
- to develop new *in situ* diagnostic techniques with surface and bulk sensitivity for studying the structural changes of various anode and cathode materials for Na batteries

✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*

- to develop in situ diagnostic techniques with surface and bulk sensitivity to improve the calendar and cycle life of batteries by studying the mechanism of capacity and power fading of Na-ion and Na metal batteries.

✓ *Diagnostics study of electrode materials with lower cost potential.*

# Milestones

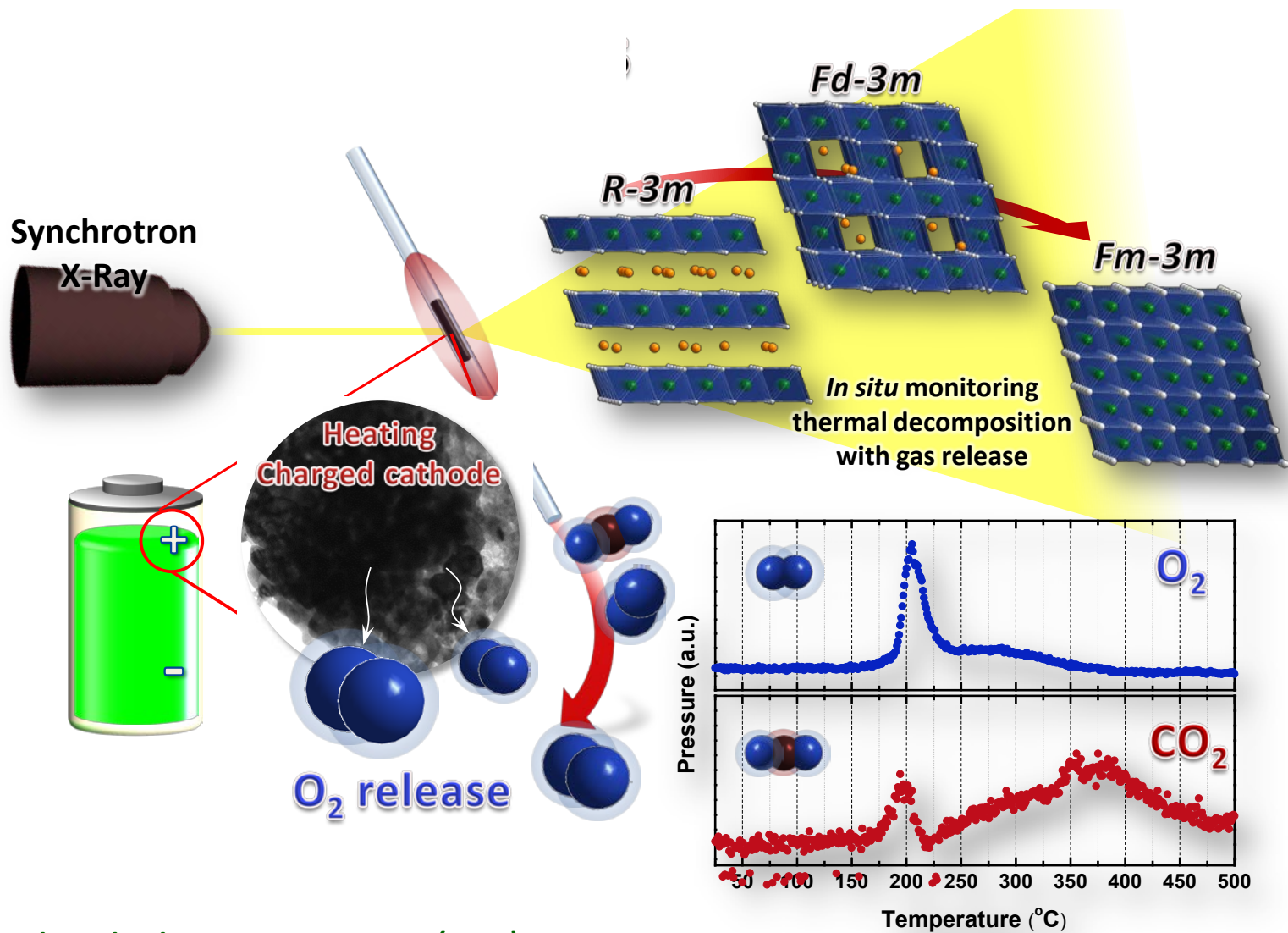
Month/Year	Milestones
Dec/15	Complete the synchrotron based in situ x-ray diffraction studies of tunnel structured $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$ as anode material for Na-ion batteries during charge-discharge cycling ➔ <b>Completed.</b>
Mar/16	Complete the in situ x-ray diffraction of the $\text{Na}_{0.66}[\text{Mn}_{0.66}\text{Ti}_{0.34}]\text{O}_2$ high capacity cathode material for Na-ion half-cell during discharge/charge cycling in a voltage range between 1.5 and 3.9 V. ➔ <b>Completed.</b>
Jun/16	Complete the synchrotron based x-ray absorption near edge structure (XANES) studies of $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$ at Ni, Co, Fe, and Ti k-edge as cathode material for Na-ion batteries during charge-discharge cycling ➔ <b>On schedule.</b>
Sep/16	Complete the synchrotron based in situ x-ray diffraction studies of $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$ as cathode material for Na-ion batteries during charge-discharge cycling ➔ <b>On schedule.</b>

# Approaches

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- A combination of time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS), together with *in situ* soft and hard X-ray absorption (XAS) during heating and transmission electron microscopy (TEM) to study the thermal stability of the Na battery electrode materials.
- Synchrotron based X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), to elucidate and differentiate the contribution from each component and element to the capacity and structural changes of various cathode and anode materials for Na-ion batteries.
- Extended collaboration with other US and international academic institutions and US industrial partners.

# In situ time-resolved XRD with mass spectroscopy



*S.-M. Bak et al., Chem. Mater. 25, 337 (2013)*

*E. Hu et al., Chem. Mater. 26, 1108 (2014)*

*S.-M. Bak et al., ACS Appl. Mater. Interfaces 6, 22594 (2014)*

# Technical Accomplishments

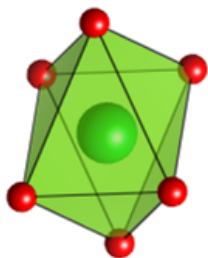
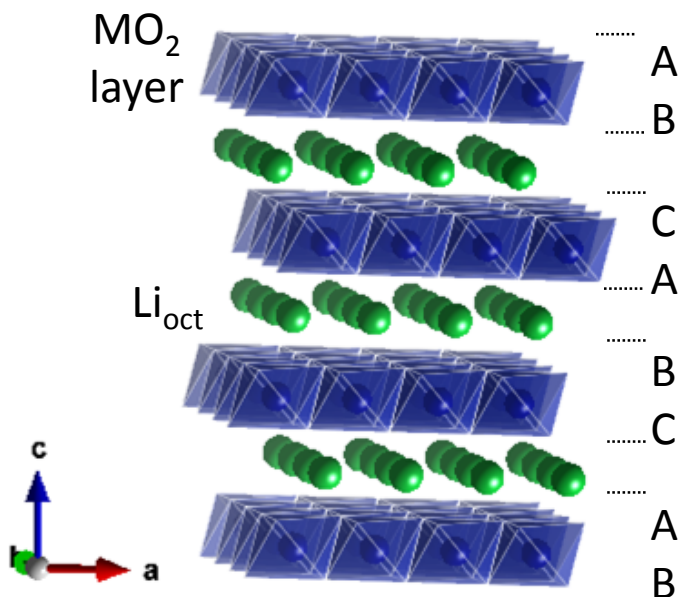
- through collaboration with Prof. Yongsheng Hu at Institute of Physics, Chinese Academy of Sciences, the structural changes in a new cathode materials  $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$  during Na insertion and extraction were studied using in situ XRD experiment. The results show continuous peak shift during Na insertion/extraction but no new phase formation upon Na insertion/extraction into/from  $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$  in a wide Na content range was observed. Although a significant amount of  $\text{Mn}^{3+}$  was reserved in  $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$  structure for the entire range of electrochemical cycles, the main crystal structure was maintained during the entire charge/discharge process without any obvious structure transformation. This is further supported by ex situ STEM results. The results of this study were published on [Nature communications](#)
- Through collaboration with Prof. Yuguo Guo at Institute of chemistry, Chinese Academy of Sciences, Structure evolution of sodium iron ferrocyanide (Prussian Blue Analogous) as cathode materials for Na-ion batteries has been studied using ex situ X-ray absorption near edge spectroscopy (XANES) and Extended X-ray absorption fine structure spectroscopy (EXAFS) at different charge or discharge states at the Fe k-edge. The energy of the absorption maximum (7,131 eV) for the fully charged electrode (4.4 V) is similar to that of the  $\text{K}_3\text{Fe}(\text{CN})_6$ , which confirms that most of Fe in the charged states are in the  $\text{Fe}^{3+}$  state. The results of this study was published on [Nano Research](#).
- Through collaboration with prof. Zhengwen Fu at Fudan University, O3-type layered transition metal oxide  $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$  as a high rate and long cycle life cathode material for sodium ion batteries has been studied using synchrotron based XRD and XAS, the results was published on [J. Mater. Chem. A](#)



# Comparing the thermal stability of charged P2-type $\text{Li}_{0.45}\text{CoO}_2$ with O3-type $\text{Li}_{0.45}\text{CoO}_2$ cathode

## O3-type ( $R\bar{3}m$ , $C2/m$ )

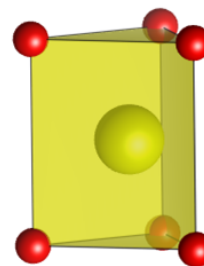
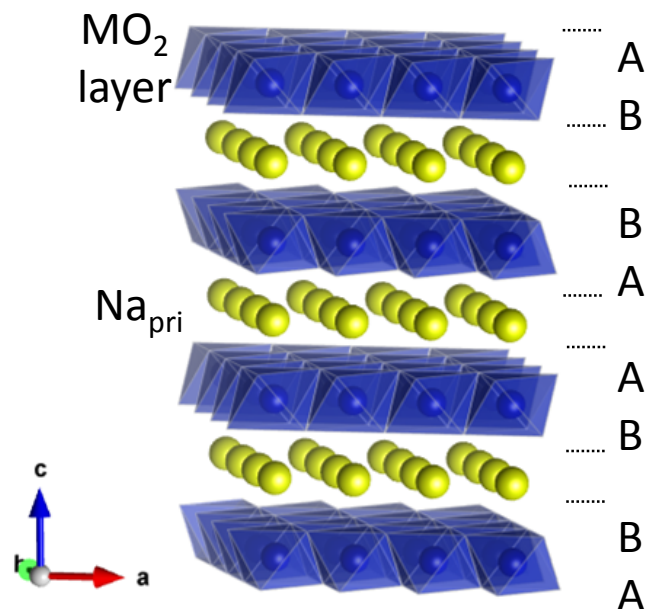
$\text{LiCoO}_2$ ,  $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ,  $\text{NaCrO}_2$ ,  $\text{NaFeO}_2$ ...



Octahedral  
site

## P2-type ( $P6_3/mmc$ )

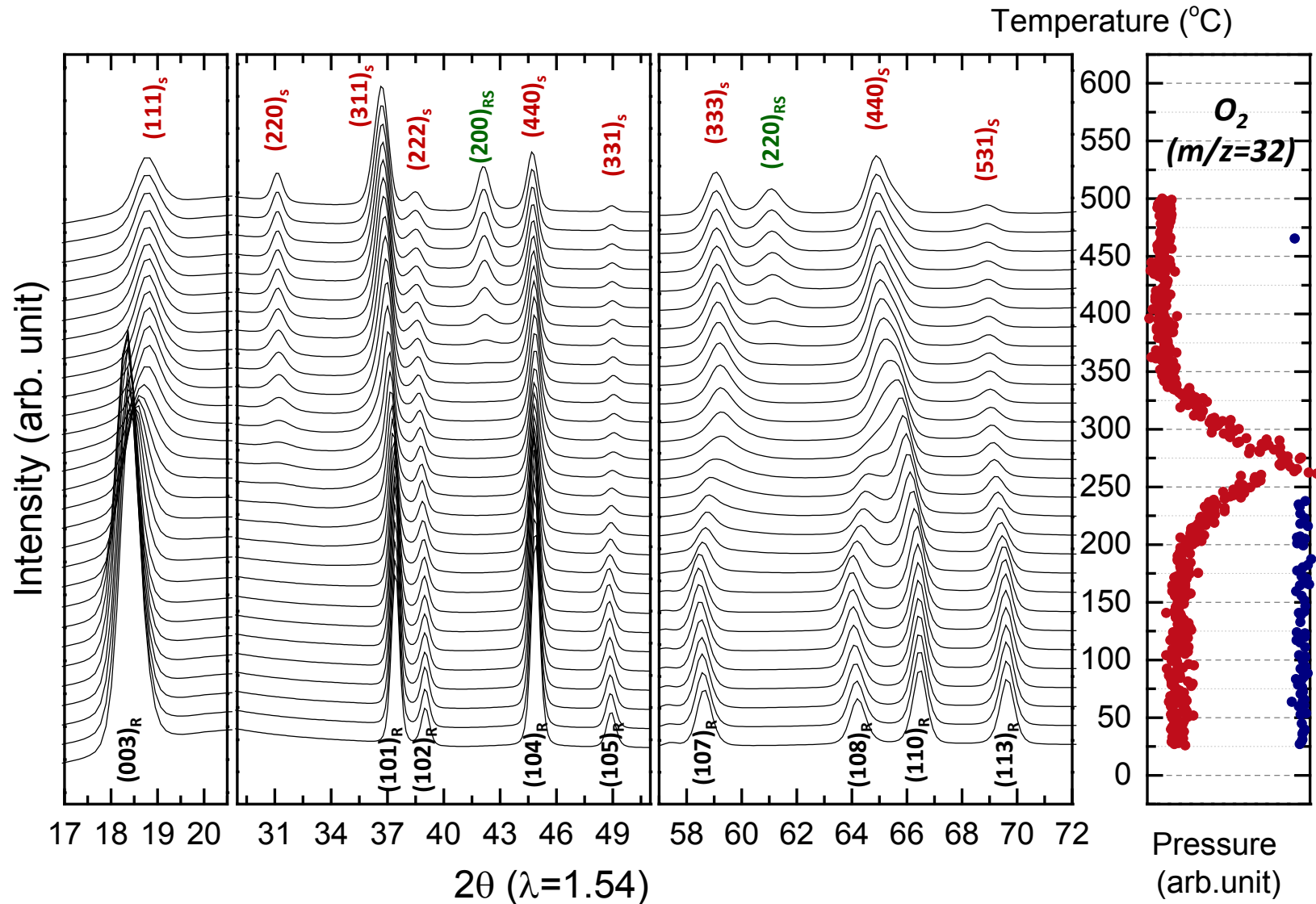
$\text{Na}_x\text{CoO}_2$ ,  $\text{Na}_x\text{MnO}_2$ ... $x=2/3$



Prismatic  
site

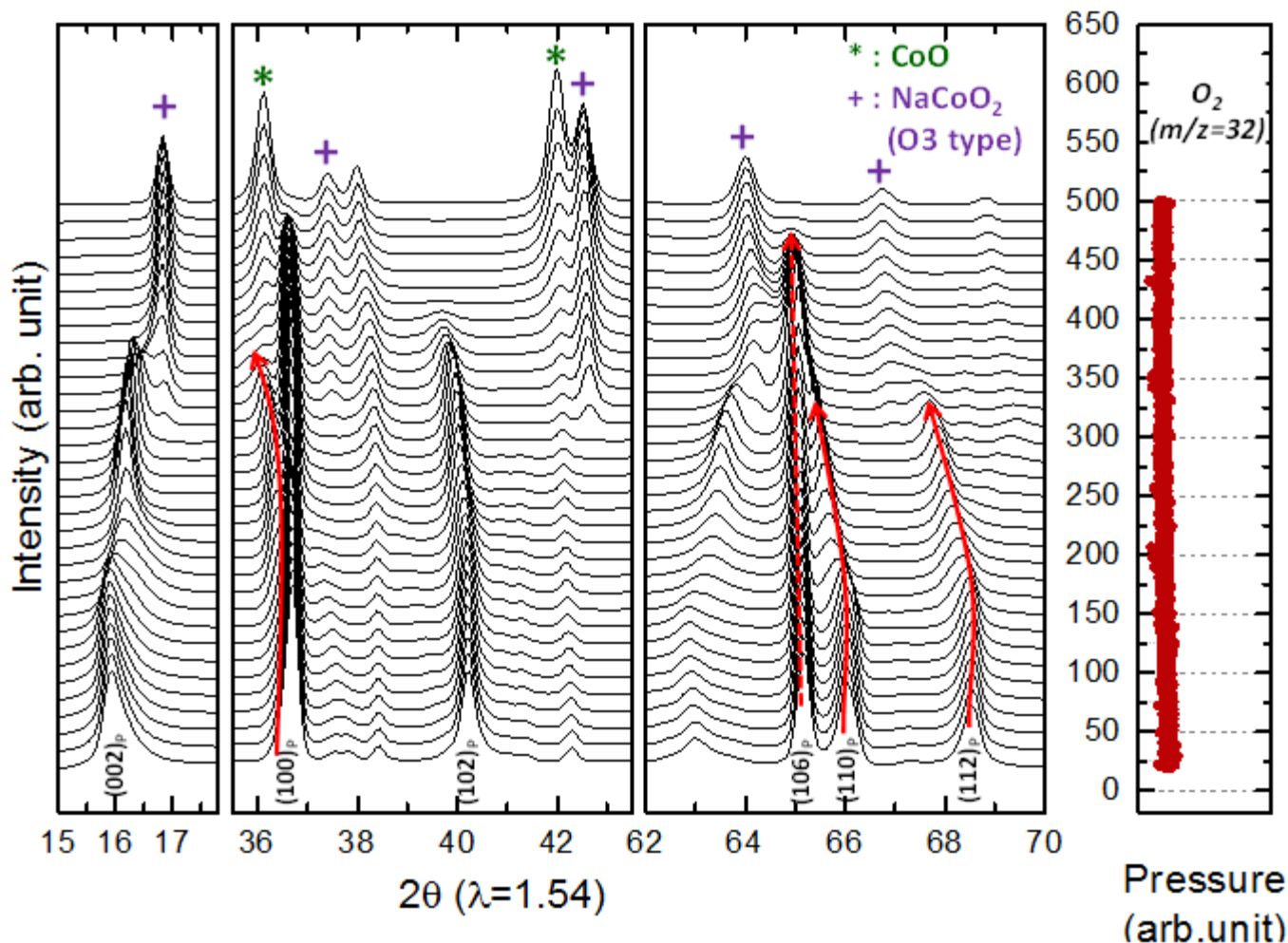


# Instability of charged O3-type $\text{Li}_{0.45}\text{CoO}_2$ cathode



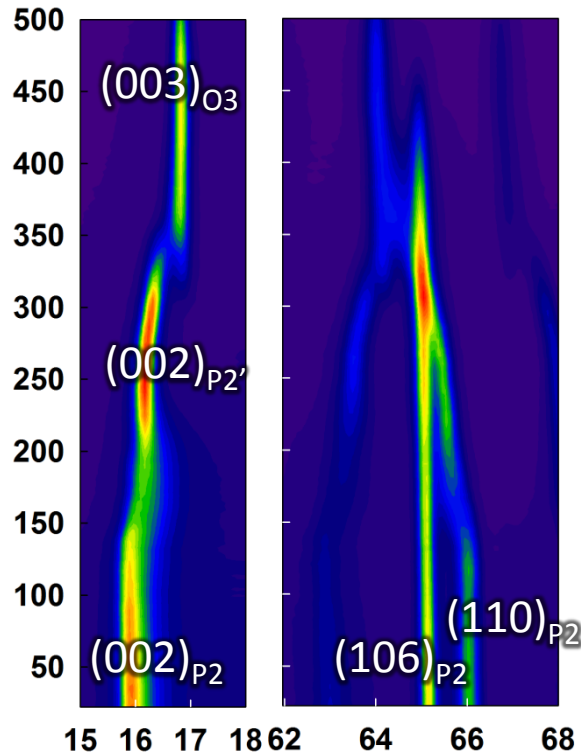
- $\text{O}_2$  gas released during phase transition from layered structure to spinel structure at 175 ~ 350  $^{\circ}\text{C}$

# Thermal stability of P2-type $\text{Na}_{0.45}\text{CoO}_2$

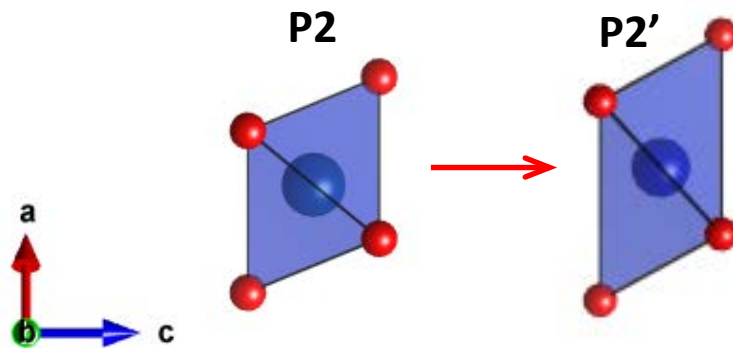


- **No oxygen release!!!**
- **P2 structure was maintained until ca. 300°C with slight changes in lattice parameters (P2→P2') and decompose to  $\text{NaCoO}_2$  (O3 type) and CoO(Rock salt).**

# Phase transition during heating: $\text{Na}_{0.45}\text{CoO}_2$



- $\text{Na}_{0.45}\text{CoO}_2$  maintained layered structure even at high temperature region, whereas  $\text{Li}_{0.45}\text{CoO}_2$  transformed to spinel-type structure  
: layer structure framework of  $\text{Na}_{0.45}\text{CoO}_2$  is very stable and not significant amount of oxygen release.
- $\text{P2} \rightarrow \text{P2}' \rightarrow \text{O3-type NaCoO}_2$   
(with a little of rock salt  $\text{CoO}$ )  
: Co does not migrate to Na layer??  
No Spinel phase!!

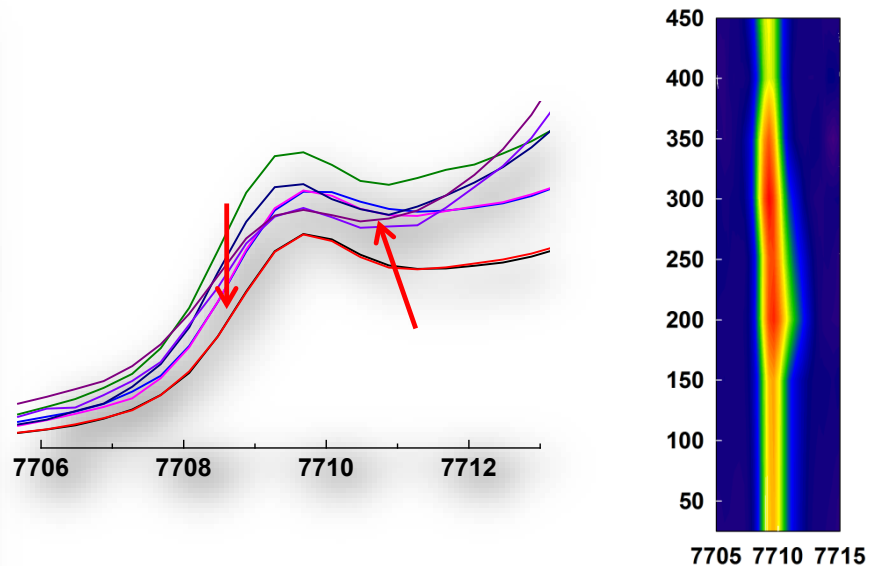
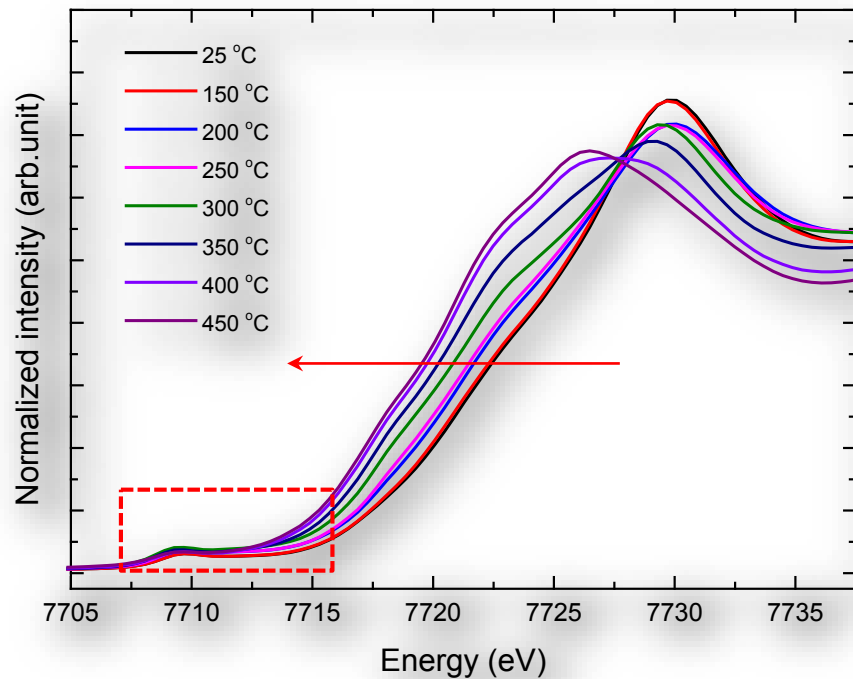


Major peak shift related to asymmetric expansion of *ab* plane and *c*-axis

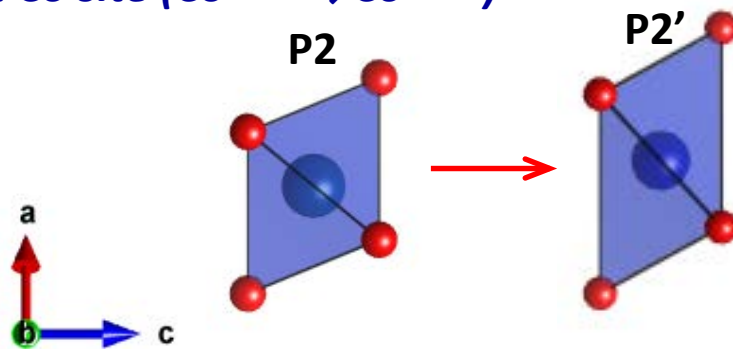
:**structural distortion!!!**

How about the **Local structure changes?**

# Reduction of Co ion during heating: XANES

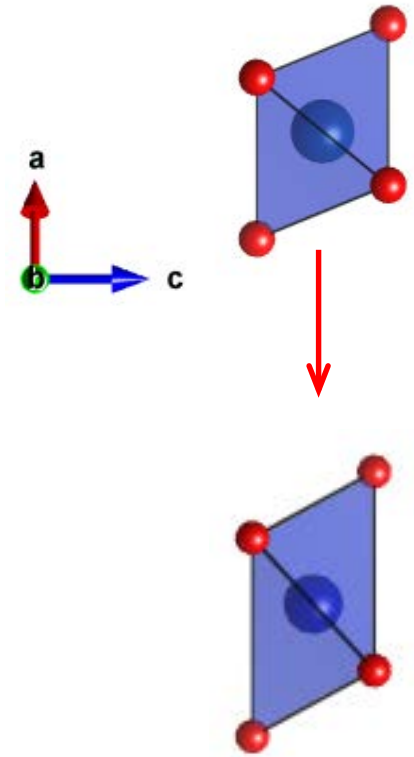
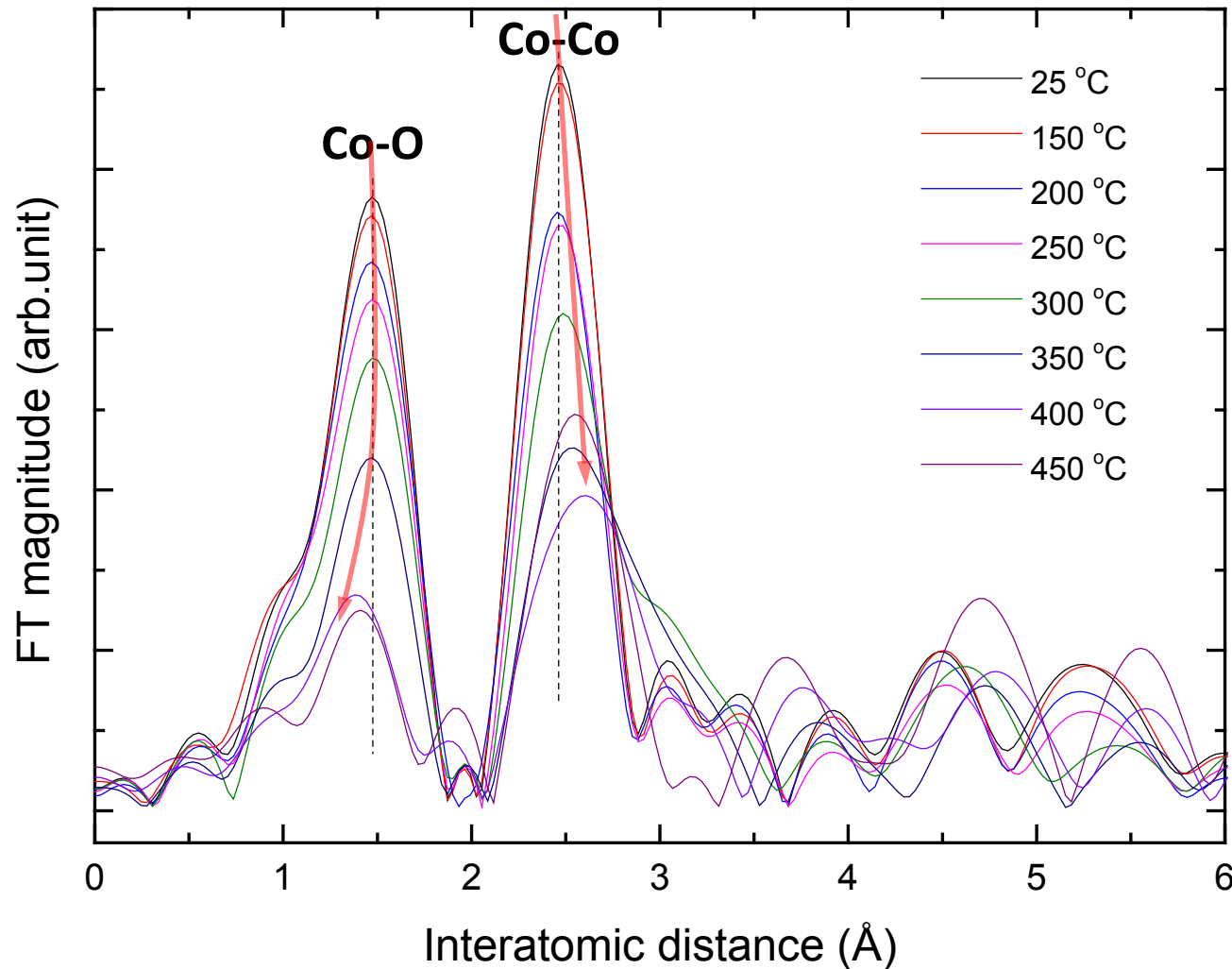


- During heating, reduction occurs at Co site ( $\text{Co}^{3+,4+} \rightarrow \text{Co}^{2+, 3+}$ )



- Pre-edge peak intensity is increased until 300 °C and decreased upon further heating.
- The increase in pre-edge peak intensity imply that the structural distortion occurred at Co site (during course of  $\text{P2} \rightarrow \text{P2}'$ )
- The decrease in pre-edge peak intensity after 300°C may due to the recovery of center of symmetry (originated from O3 type  $\text{NaCoO}_2$ )

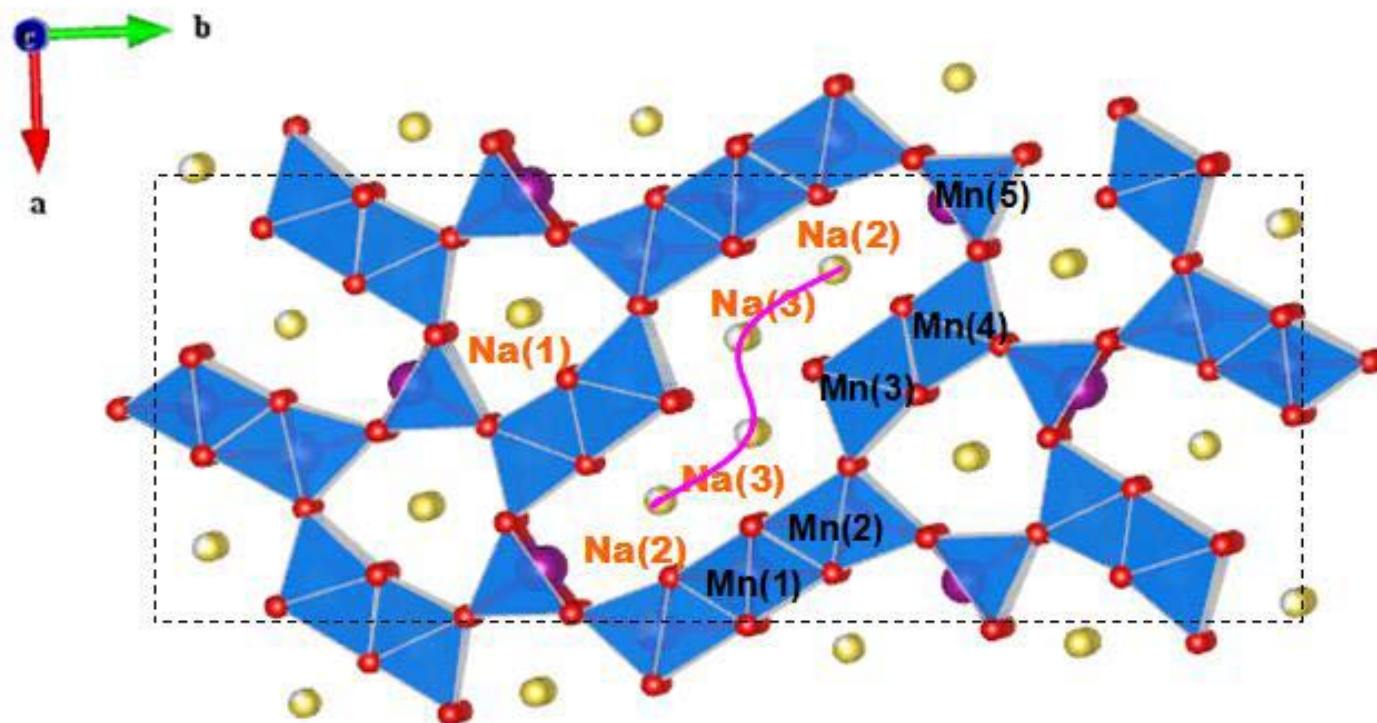
# Local structure changes of P2-type $\text{Na}_{0.45}\text{CoO}_2$ : EXAFS



**At 25 ~ 350 °C :**

**No change in average Co-O bond length and increase in average Co-Co bond length  
→ Distortion of  $\text{CoO}_6$   
(coincident with the XRD data, and pre-edge intensity change)**

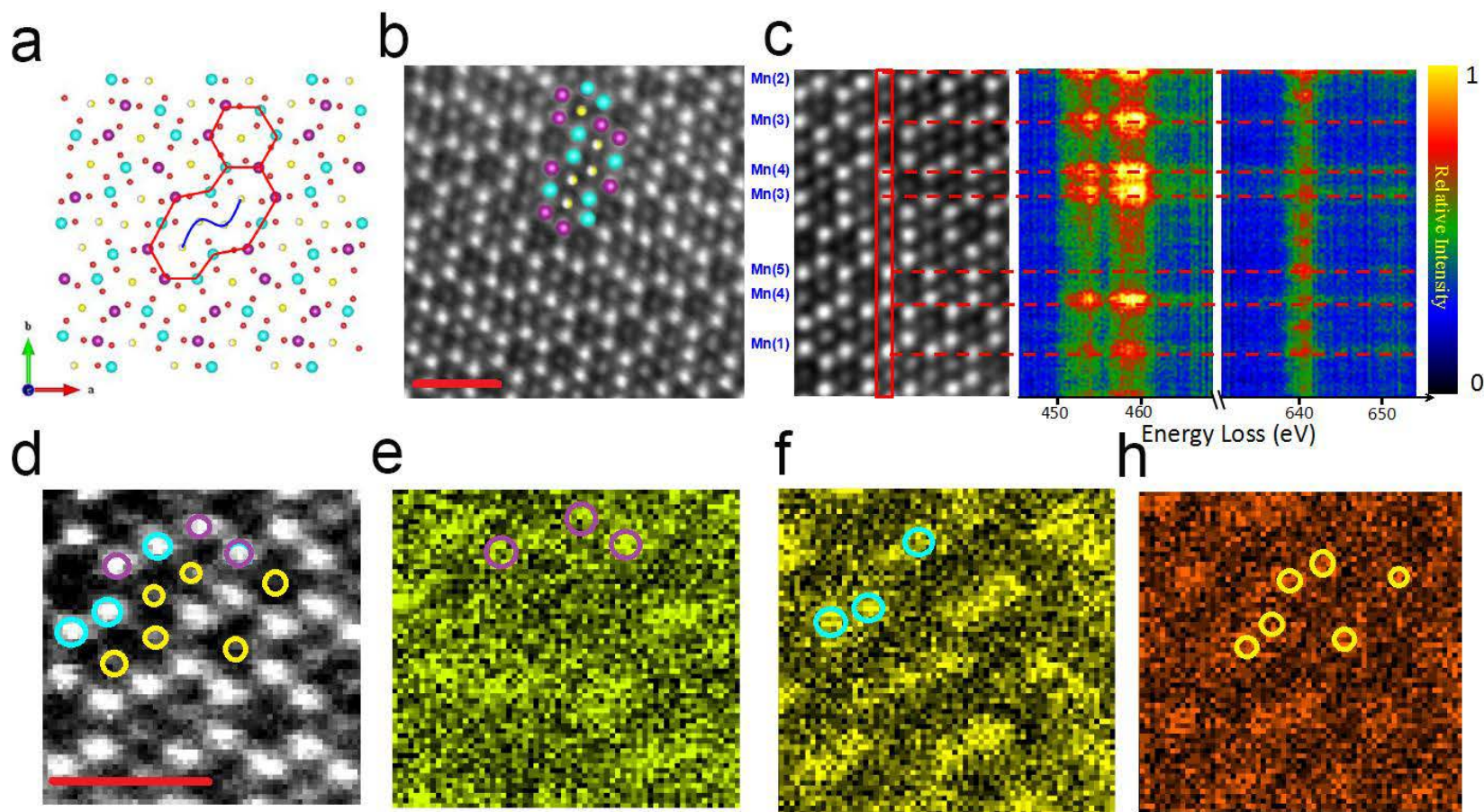
# Structural evolutions of Ti substituted tunnel-type $\text{Na}_{0.44}\text{MnO}_2$ oxide as anode materials for aqueous sodium-ion batteries



Crystal Structure of  $\text{Na}_{0.44}\text{MnO}_2$



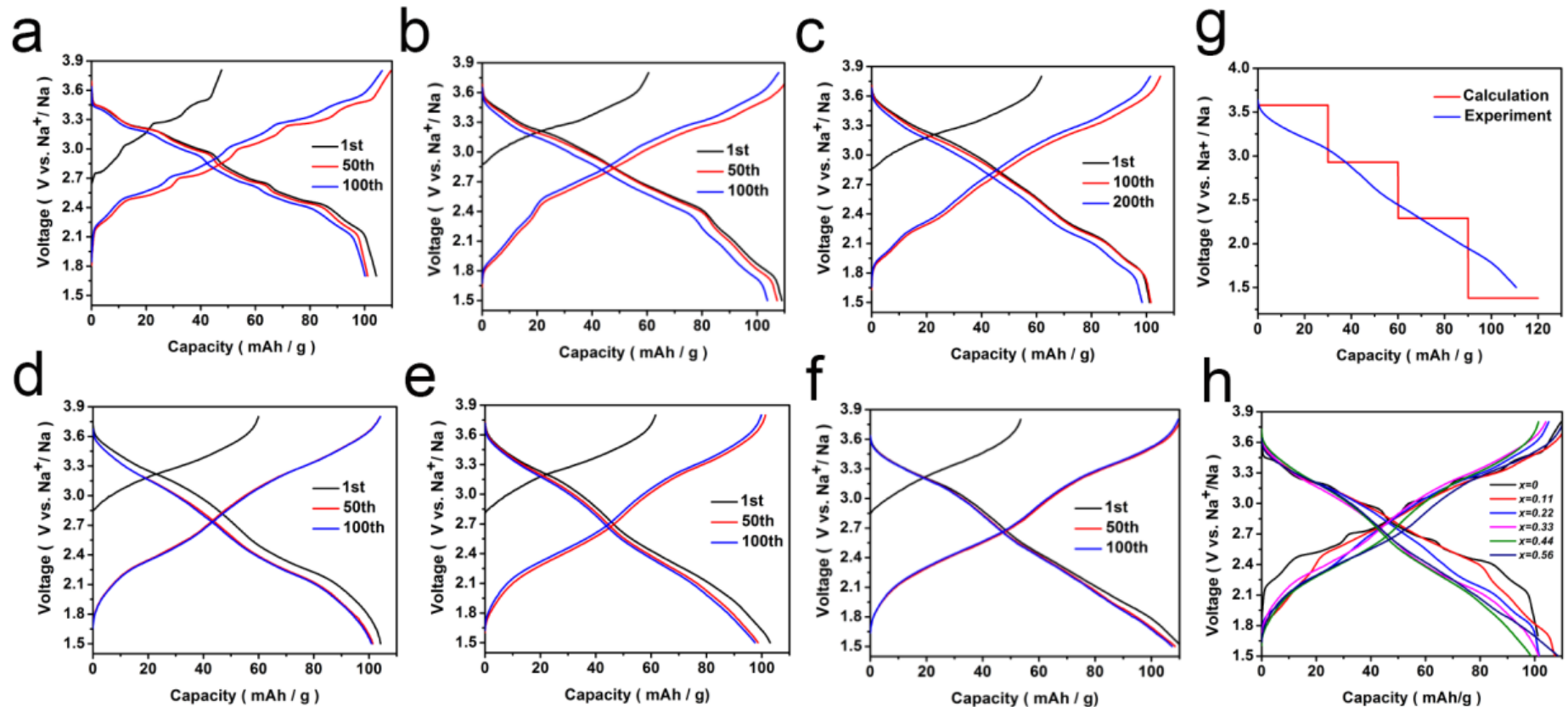
# STEM images of $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$



(a) General view of the crystal structure and view along [010] zone axis. (b) HAADF-STEM image for the as-prepared  $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$  materials along [010] zone axis. Scale bar, 2 nm. (c) The EELS image of  $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$ . The EDS mapping, (d) HAADF-STEM image, (e-h) the corresponding elemental mapping of the Mn, Ti and Na elements, respectively. Scale bar, 2 nm.

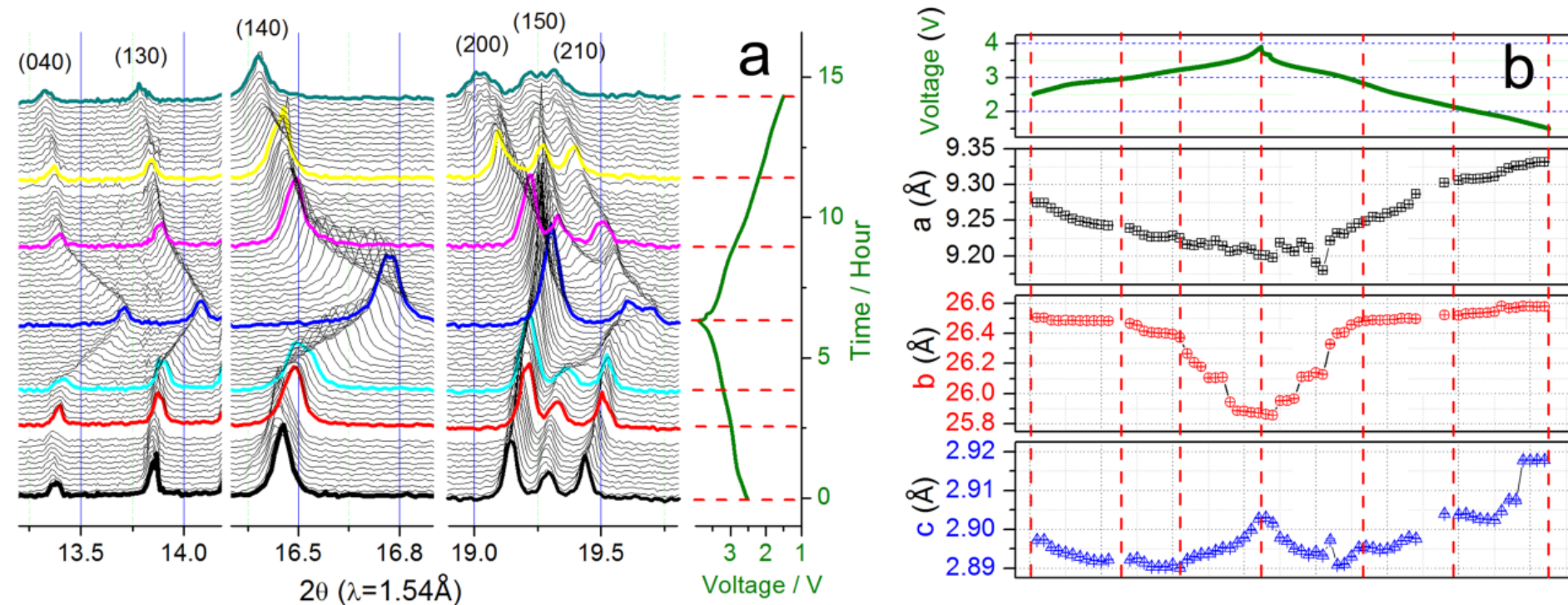


# Sodium storage performance of $\text{Na}_{0.44}[\text{Mn}_x\text{Ti}_{1-x}]\text{O}_2$ electrodes in non-aqueous solution



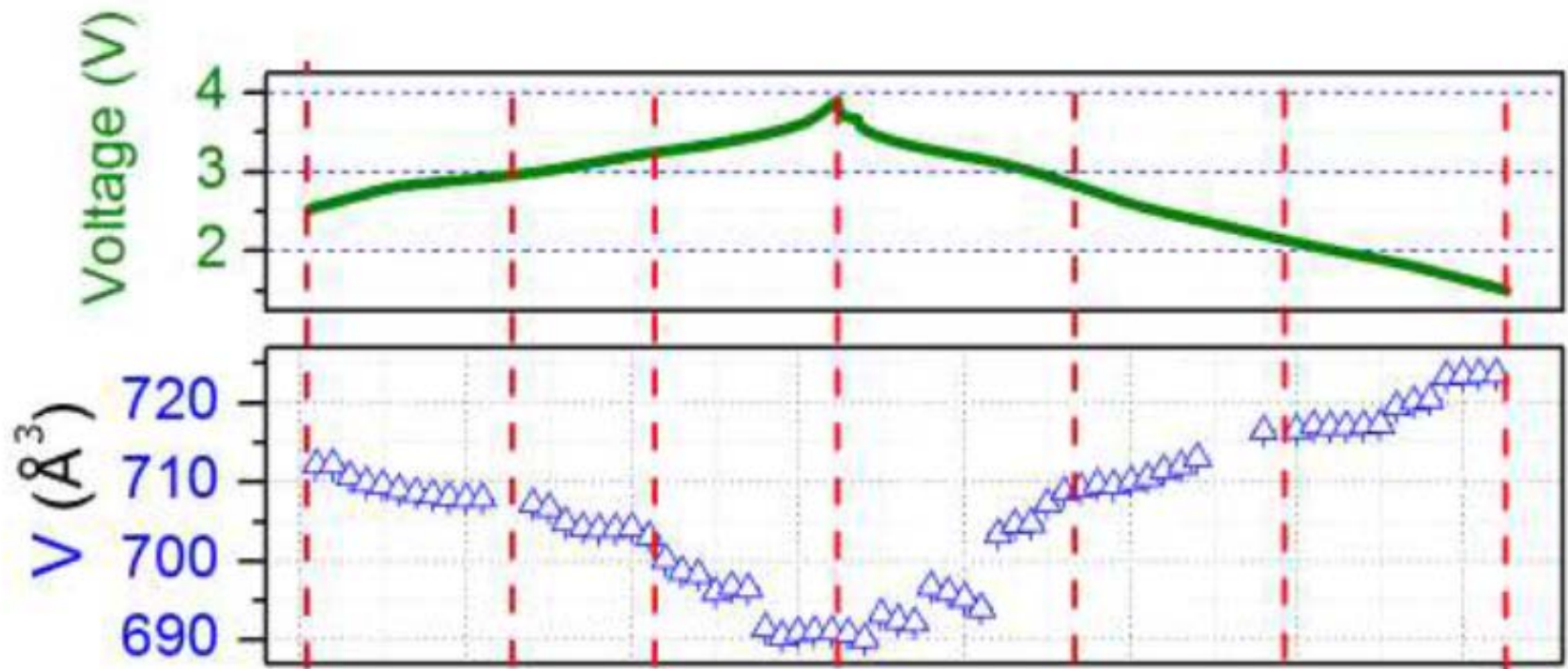
The 1<sup>st</sup>, 50<sup>th</sup> and 100<sup>th</sup> discharge/charge curves at a current rate of C/10 in the voltage range of 1.5 and 3.8 V versus  $\text{Na}^+/\text{Na}$ . (a)  $\text{Na}_{0.44}\text{MnO}_2$ , (b)  $\text{Na}_{0.44}[\text{Mn}_{0.89}\text{Ti}_{0.11}]\text{O}_2$ , (c)  $\text{Na}_{0.44}[\text{Mn}_{0.78}\text{Ti}_{0.22}]\text{O}_2$ , (d)  $\text{Na}_{0.44}[\text{Mn}_{0.67}\text{Ti}_{0.33}]\text{O}_2$ , (e)  $\text{Na}_{0.44}[\text{Mn}_{0.56}\text{Ti}_{0.44}]\text{O}_2$ , (f)  $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$ . (g) Comparison of DFT calculated voltage curve and experiment curve for the  $\text{Na}_x[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$  electrode

# Structure evolution of $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$ upon Na extraction/insertion

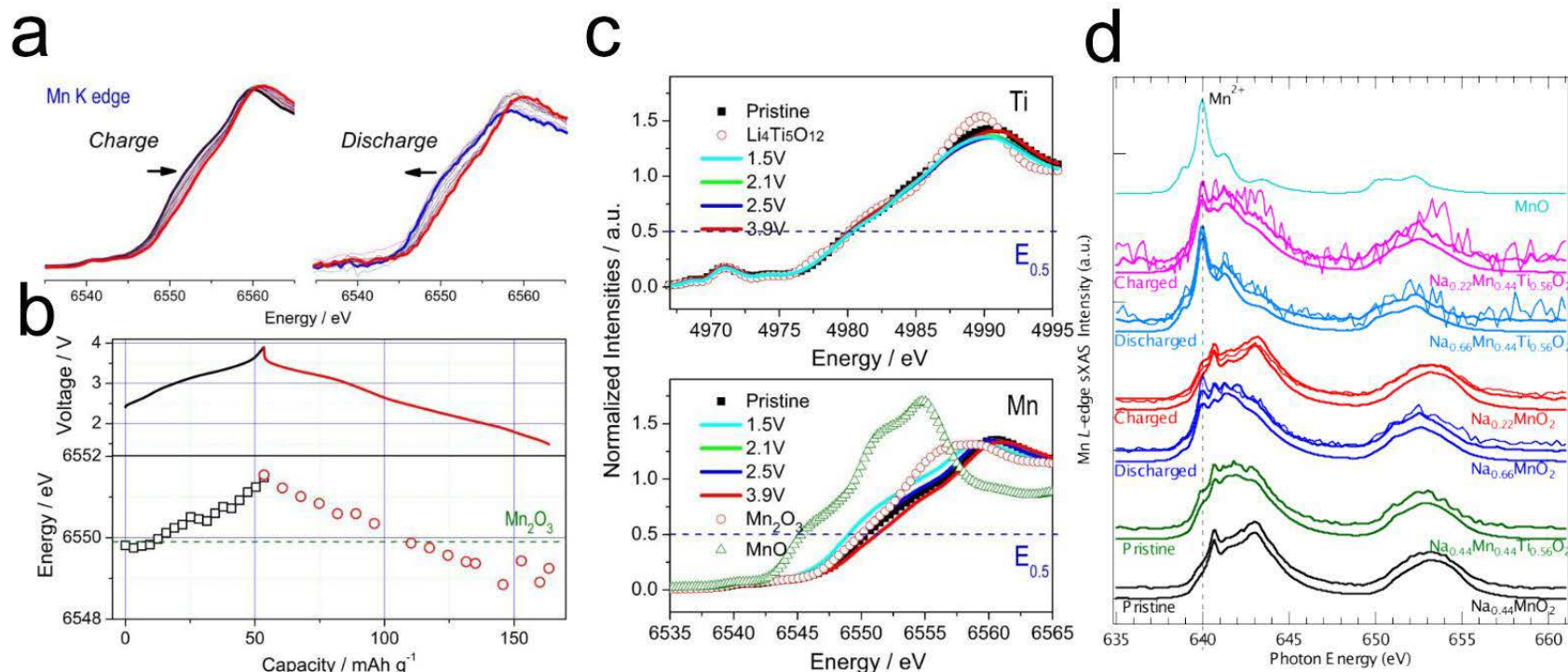


(a) *In situ* XRD patterns collected during the first discharge/charge of the  $\text{Na}/\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$  cell under a current rate of C/10 at a voltage range between 1.5 and 3.9 V. For easy comparison with results in the literature, the  $2\theta$  angle has been converted to values corresponding to the more common laboratory Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). (b) Evolution of the Lattice parameters during charge/discharge process

# Unit cell evolution of $\text{Na}_{0.44}[\text{Mn}_x\text{Ti}_{1-x}]\text{O}_2$ upon Na extraction/insertion



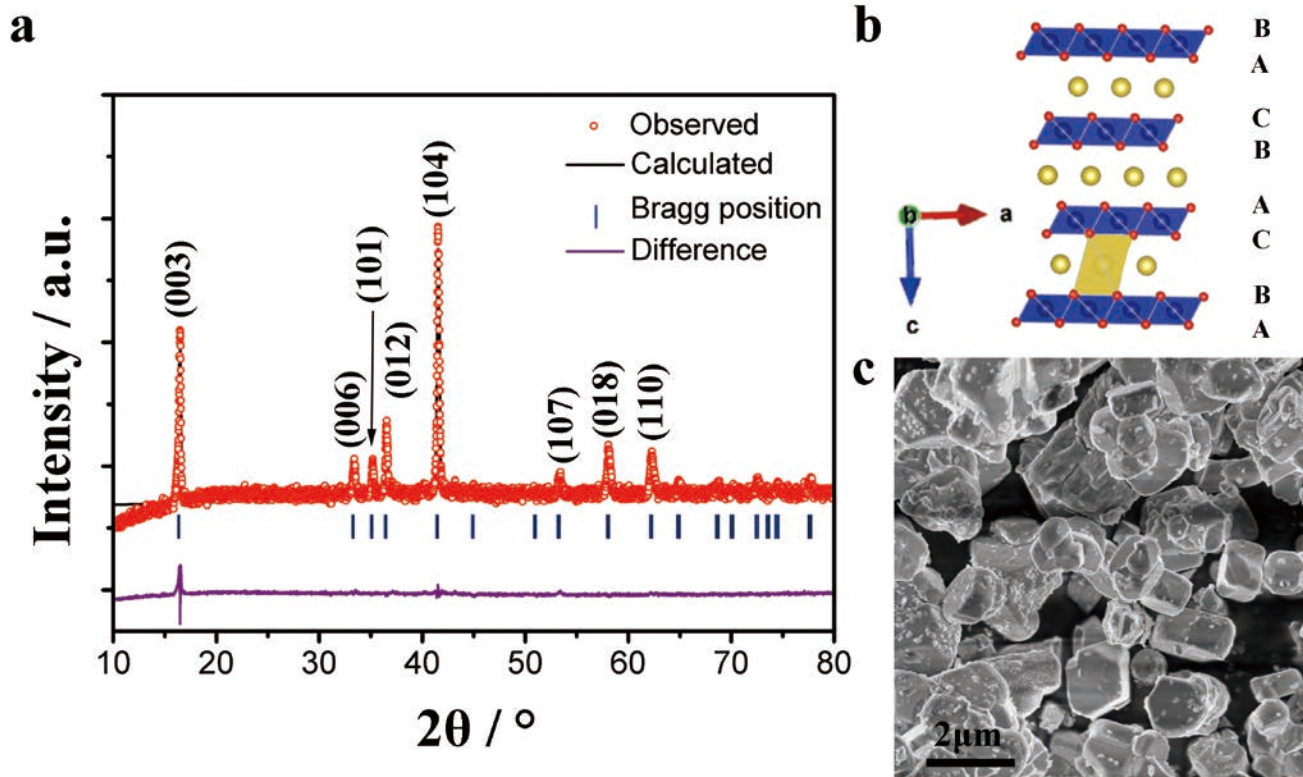
# Charge transfer mechanism of $\text{Na}_{0.44}[\text{Mn}_x\text{Ti}_{1-x}]\text{O}_2$ upon Na extraction/insertion



(a) In situ X-ray absorption spectra at Mn K-edge XANES spectra collected during initial charge and discharge at a current rate of C/8 between 1.5 and 3.9 V voltage range (Data are obtained in two different in situ cells for charge and discharge process separately); (b) Variation of Mn K-edge position during initial charge and discharge; (c) Ti and Mn K-edge XANES spectra ex situ collected at different charge/discharge states. Spectra of reference materials were represented for comparison. (d) Mn L-edge sXAS spectra collected on Na<sub>x</sub>MnO<sub>2</sub> and Na<sub>x</sub>[Mn<sub>0.44</sub>Ti<sub>0.56</sub>]<sub>2</sub>O samples with x = 0.22, 0.44 and 0.66, as well as on the MnO reference sample.

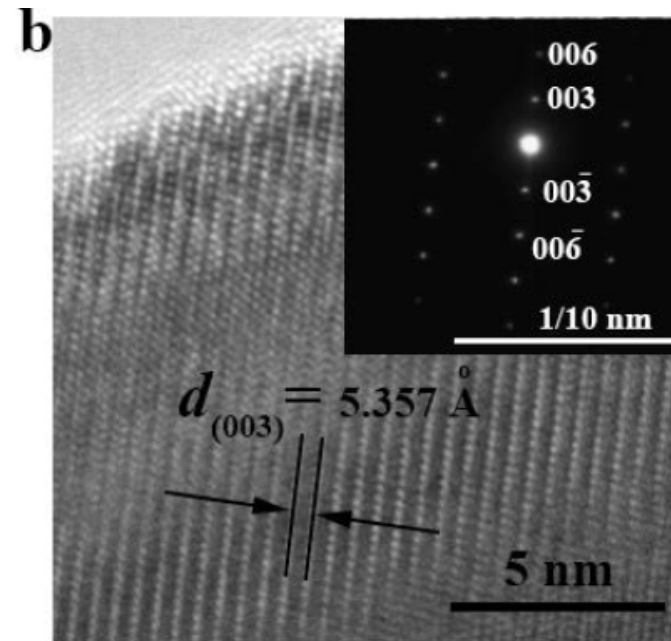
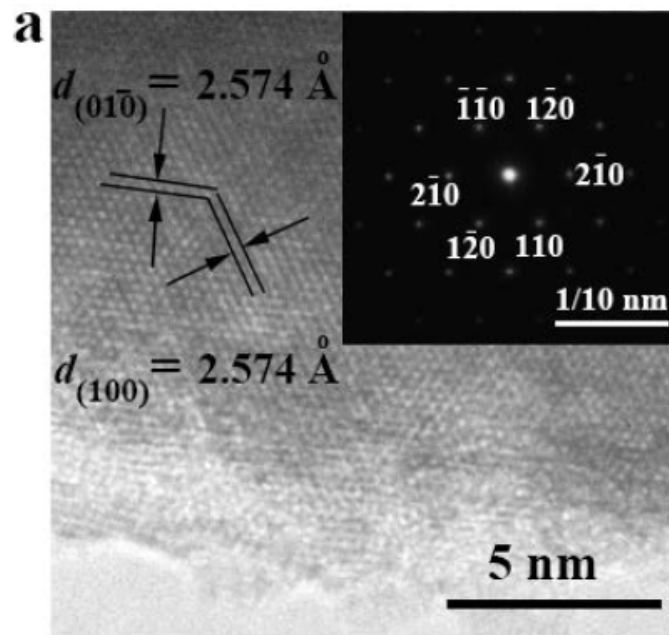


# O3-type Layered Transition Metal Oxide $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$ as a High Rate and Long Cycle Life Cathode Material for Sodium Ion Batteries



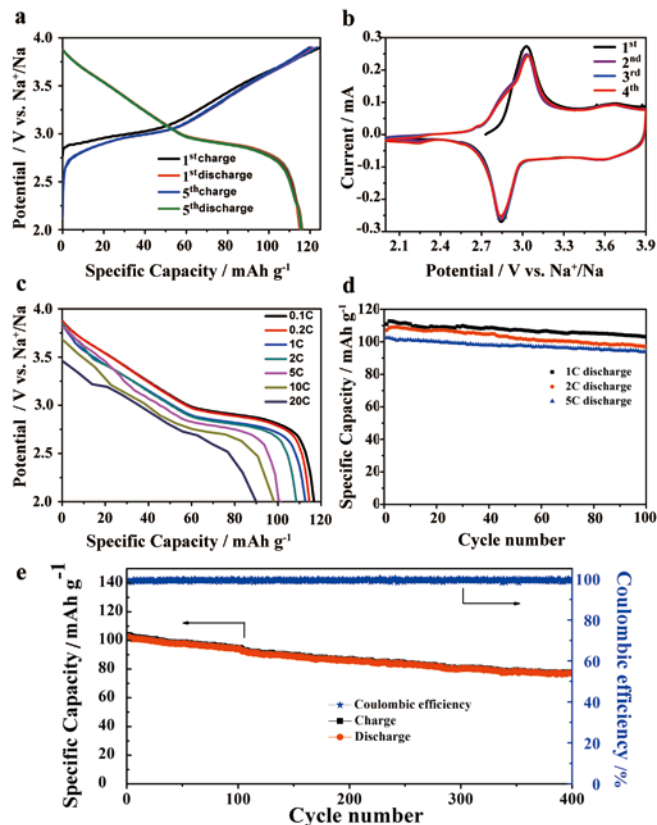
(a) X-ray diffraction pattern and Rietveld refinement of the as-prepared O3- $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$  (NCFT) sample. (b) Schematic of the O3-NCFT crystal structure, legend: red, blue and yellow balls stand for oxygen, transition metal and sodium ions, respectively. (c) SEM image of the O3-NCFT material.

# HRTEM images and SAED patterns (insets) of the O3-NCFT



HRTEM images and SAED patterns (insets) of the O3-NCFT material acquired from the (a) [001] and (b) [100] zone axis..

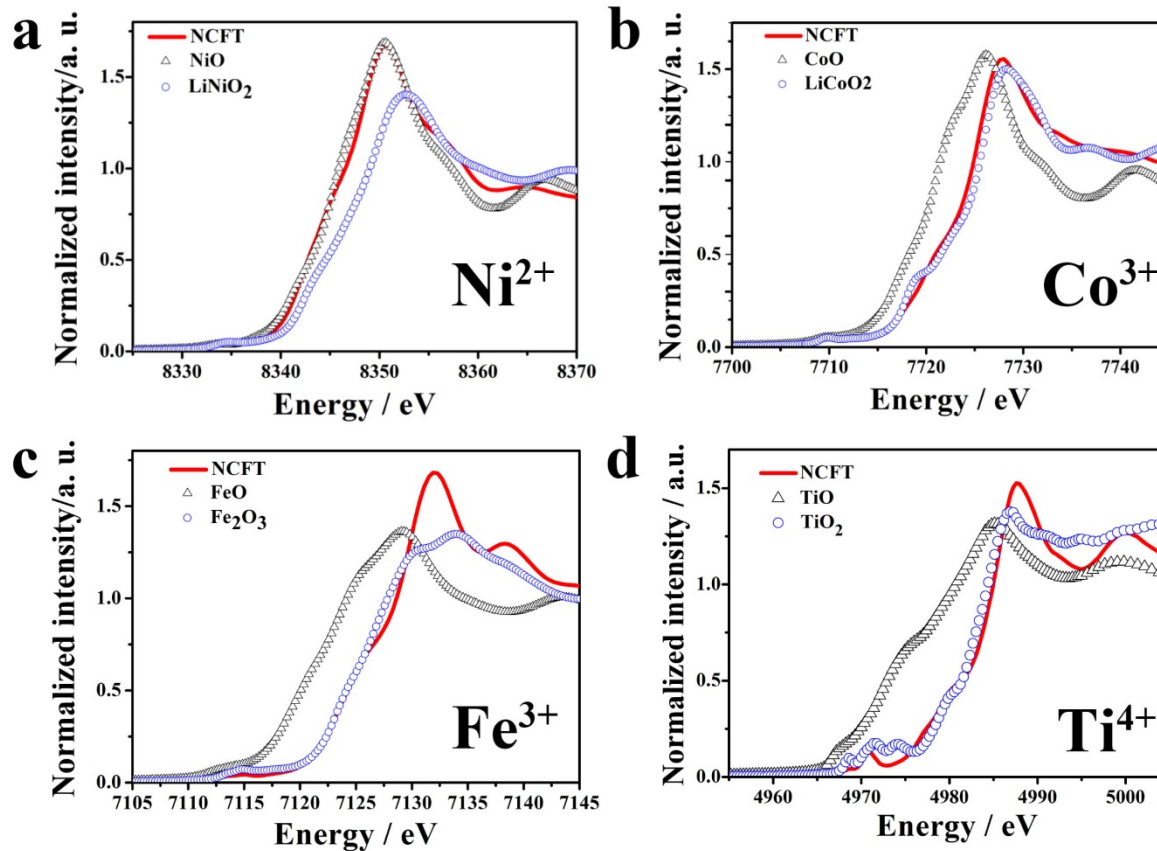
# The charge-discharge curves and cycle performance of $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$ as Cathode Material for Sodium Ion Batteries



(a) The galvanostatic charge/discharge curves of O3-NCFT in the initial five cycles at 0.1C rate in the potential range of 2.0 - 3.9V versus  $\text{Na}^+/\text{Na}$ , (b) the initial four cyclic voltammograms between 2.0 and 3.9 V versus  $\text{Na}^+/\text{Na}$  at the scan rate of  $0.1 \text{ mV s}^{-1}$ , (c) Rate capability at various current rates, (d) Cyclic performances at 1C, 2C and 5C rates. (e) Long term cyclic performances of the O3-NCFT electrode cycled at a current density 5C.



# XANES spectra at the K-edges of Ni Co Fe and Ti of pristine NCFT and corresponding metal oxides references.



XANES spectra at the (a) Ni, (b) Co, (c) Fe and (d) Ti K-edges of pristine NCFT and corresponding metal oxides references.

# Response to last year reviewer's comments

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Comments from 2015 AMR

Response

Project was not reviewed in 2015AMR

Project was not reviewed in 2015AMR

# Collaborations with other institutions and companies

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- **Lawrence Berkeley National Laboratory**  
Sodiation Kinetics of Metal Oxide Conversion
- **University of Maryland at College Park**  
Sodiation Kinetics of Metal Oxide Conversion
- **Drexel University**  
Probing the mechanism of high capacitance sodium anode materials in 2D titanium carbides
- **University of Texas-Austin**  
Removal of interstitial H<sub>2</sub>O in hexacyanometallates for a superior sodium battery cathode
- **Massachusetts Institute of Technology (MIT)**  
A quaternary layered cathode compound for rechargeable Na ion batteries
- **Institute of Chemistry, Chinese Academy of Sciences**  
*In situ* XRD and XAS study of cathode materials for sodium batteries
- **Institute of Physics, Chinese Academy of Sciences**  
Studies on new cathode and anode material for sodium batteries using *in situ* XRD and XAS
- **Fudan University, Shanghai, China**  
*In situ* XRD and XAS study of cathode materials for sodium batteries

# Remaining Challenges and Barriers

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- The cathode and anode materials widely used for Li-ion batteries can not be simply applied to sodium and Na-ion batteries, since the intercalation and transport mechanism for Na is quite different than for Li. New cathode and anode materials for Na batteries need to be developed and characterized.
- The relationships between the structural changes and the performance of sodium batteries has been extensively studied but the fundamental understanding of this relationship still need to be further enhanced. The advanced tools need to be developed for such studies.
- Morphology and elemental mapping of anode and cathode materials are needed as diagnostic tools for sodium battery research. The full field transmission x-ray microscopy (TXM) technique as well as micro- and nano- probe scanning TXM need to be developed for battery research.

# Proposed Future Work for *FY 2016* and *FY2017*

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## ■ FY2016 Q3 Milestone:

Complete the synchrotron based x-ray absorption near edge structure (XANES) studies of  $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$  at Ni, Co, Fe, and Ti k-edge as cathode material for Na-ion batteries during charge-discharge cycling .

## ■ FY2016 Q4 Milestone:

Complete the synchrotron based in situ x-ray diffraction studies of  $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$  as cathode material for Na-ion batteries during charge-discharge cycling.

## FY2017 work proposed:

- Synchrotron based XRD and XAS, as well as pair distribution function (PDF) techniques will be applied to study the new  $\text{NaMnCuO}_2$  cathode materials for Na-ion batteries
- The full field transmission x-ray microscopy (TXM) technique as well as micro- and nano- probe scanning TXM techniques will be developed and applied for Na battery research to study the element distribution of new NASICON based solid electrolyte materials for Na batteries.
- The collaborative research with US academic research institutions and industrial partners will be further expanded and strengthened.

# Summary

## ■ Relevance

- ✓ *Diagnostics study of thermal stability of Na cathode materials in comparison with Li-ion materials (to improve the **safety** characteristics).*
- ✓ *Synthesis and characterization studies aimed to improve the calendar and cycle **life** of Na-ion batteries through exploring the new cathode and anode materials with desired structures and chemical compositions.*
- ✓ *Diagnostics study of new electrode materials with lower **cost** potential.*

## ■ Approaches

- *Time resolved X-ray diffraction (TR-XRD) and mass spectroscopy (MS)*
- *In situ x-ray diffraction and absorption spectroscopy*
- *Synchrotron based x-ray pair distribution function (PDF)*
- *Full field as well as micro- and nano- probe scanning TXM*
- *High resolution transmission electron microscopy (HR-TEM)*

## ■ Technical Accomplishments

- *Completed thermal stability studies of Charged P2-type  $\text{Na}_{0.45}\text{CoO}_2$  showing no major phase transition up to 300 °C with better thermal stability than  $\text{Li}_{0.45}\text{CoO}_2$ .*
- *Completed in situ XRD studies on  $\text{Na}_{0.44}[\text{Mn}_{0.44}\text{Ti}_{0.56}]\text{O}_2$  anode materials*

## ■ Proposed Future work

- *Continue and complete the XAS and XRD studies of  $\text{Na}(\text{NiCoFeTi})_{1/4}\text{O}_2$*
- *Develop and apply the full field transmission x-ray microscopy (TXM) as well as micro- and nano- probe scanning TXM techniques for battery materials to study the solid electrolyte materials of Na batteries*
- *Develop and apply the synchrotron based PDF technique for sodium battery material studies*